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Phthalate acid esters (PAEs) accumulation in coastal sediments from regions with different land use configuration along the Persian Gulf

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ABSTRACT

Phthalate acid esters (PAEs) are widely used as plasticizers in various plastic products and have aroused considerable concern over their ubiquitous presence and potentially hazardous effects on the environment. This research provides the first data on PAEs distribution in the sediments of northern part of the Persian Gulf. To determine the concentration of 16 PAEs, 26 samples of sediments were collected from industrial stations (IS), urban stations (US), agricultural stations (AGS), and natural field stations (NS) from Asalouyeh Harbor coasts from Nov 2016 to Jan 2017. The mean values of Σ16PAEs in the samples taken from IS, AGS, US, and NS were 78.08, 11.69, 46.56, and 5.180 μg/g, respectively. The results indicated that the mean concentrations of Σ16PAEs in the samples taken from IS and AGS areas were significantly higher ($p < 0.05$) than the ones taken from US and NS areas. The order of PAEs concentrations in sediment samples were as di(2-ethylhexyl) phthalate (DEHP), di-n-butyl phthalate (DnBP), butylbenzyl phthalate (BBP), and di-*n*-octyl phthalate (DnOP), respectively. DEHP was detected in all collected samples and the mean ± SD of its concentration in the IS, US, AGS, and NS regions were as 28.15 ± 4.9, 4.040 ± 0.53, 11.58 ± 1.2, and 1.780 ± 0.78 μg/g, respectively. The major sources of PAEs in the sediments collected from the study region were associated with the industrial and agricultural activities. The findings of this study indicated that the sediments of the Asalouyeh coasts are heavily contaminated with PAEs. They have shown potential ecotoxicological effects on the aquatic organisms and benthic. Therefore, more attention should be paid to prediction of the marine ecosystem in this region by the authorities.

1. Introduction

The issue of environmental contamination and degradation is of the most important and serious problems' resulting from human generation in today's world, and have changed into a hot topic for study by researchers (Hashemi et al., 2017; Karimaei et al., 2017; Jafari et al.,

Abbreviation: PAEs, Phthalate acid esters; DMP, Dimethyl phthalate; DEP, Diethyl phthalate; DnBP, Di-n-butyl phthalate; BBP, Butylbenzyl phthalate; DEHP, Di(2-ethylhexyl) phthalate; DnOP, Di-*n*-octyl phthalate; DiBP, Diisobutyl phthalate; DMGP, Dimethylglycol phthalate; DMPP, Di(4-methyl-2-pentyl) phthalate; DEEP, Di (2-ethoxyethyl) phthalate; DnAP, Di-n-amyl phthalate; DnHP, Di-nhexylphthalate; HEHP, Di(hexyl-2-ethylhexyl) phthalate; DBEP, Di(2-n-butoxyethyl) phthalate; DCHP, Dicyclohexyl phthalate; DnNP, Di-*n*-nonyl phthalate; PVC, Polyvinylchloride; AIEH, American Institute for environment and health; PSEEZ, Pars Special Energy Economic Zone; IS, Industrial stations; AGS, Agricultural stations; US, Urban stations; NS, Natural fields stations; EC, Electrical conductivity; SIM, Selective ion monitoring; GC/MSD, Gas chromatography with mass selective detection; LOD, Limit of detection; LOQ, Limit of quantification; PCA, Principal component analysis; TOC, Total organic carbon; DF, Detection frequency; SQG, Sediment quality guideline; TEL, Threshold effect level; PEL, Probable effect level; MPC, Maximum permissible concentration; SRC_{eco}, Ecotoxicological Serious Risk Concentrations; ERL, Environmental risk levels

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2017; Dobaradaran et al., 2018, 2010; Saeedi et al., 2017; Karbasdehi et al., 2017; Babaahmadi et al., 2017). Phthalate acid esters (PAEs) are a group of chemical compounds which are mostly used for enhancing the flexibility and softness of industrial polymers. Their most important usage belongs to synthesis of polyvinylchloride (PVC), cellulose, rubber, and styrene materials (Qureshi et al., 2014; Heudorf et al., 2007). Approximately 6 million tons of PAEs are produced around the world every year (Jin et al., 2015). They are widely used in different consumer products such as packaging, buying and garbage bags, cosmetics, care products, color, glue, photography films, and insect repellents (Xu et al., 2008; Chen et al., 2017a). As these compounds do not react chemically with the molecular bonds of plastic polymers, and exist in free phase and leachable, thus they can enter the environment directly and indirectly during production, usage, and discharge of plastic materials (Wang et al., 2013). Extensive use of phthalate-containing products has led to elevated levels of PAEs in a wide range of environmental matrices such as air (Cousins et al., 2014), water and sediments of rivers and seas (Zeng et al., 2008), soil (Wu et al., 2015), wastewater (Dargnat et al., 2009), foods and drinks (Sakhi et al., 2014; Moazzen et al., 2017), biota (Blair et al., 2009), and even the urine, sperm, and amniotic fluid samples of human (Calafat et al., 2006).

With regards to the adverse health effects, a series of experimental studies on animals have shown that some metabolites of PAEs are estrogenic, and have damaging effects on endocrine glands (Chen et al., 2011). For example, the American Institute for environment and health (AIEH) has placed diethyl hexyl phthalate, dibutyl phthalate, and butyl benzyl phthalate in the group classification 1 (compounds that are able to impair endocrine glands and body metabolism) (Botham and Holmes, 2005). Also, long-term exposure to these compounds can contribute to some cancers associated with the endocrine system including breast cancer in women and prostate cancer in men (López-Carrillo et al., 2010). Moreover, some other studies have shown that PAEs and their metabolites act as anti-androgens in the pre-natal period, causing reproductive and developmental toxicities in animals (Liu et al., 2010). Accordingly, today PAEs are considered as one of the widest classes of refractory organic contaminants, whose occurrence, fate, and potential ecological risks in the environment have attracted a great deal of attention.

Aquatic environments especially river and estuarine systems receive significant amounts of chemicals through surface runoff, wastewater discharge, and atmospheric precipitation, which seriously threatening aquatic ecosystems (Li et al., 2017; Dobaradaran et al., 2017a). The ubiquity and the slow photolysis and hydrolysis rates of PAEs determine their potential to bio-accumulate in aquatic organisms and has drawn scientific interest, especially with regard to the ecotoxicity of these compounds for microorganisms, invertebrates, algae, fish, and shrimp in saltwater or freshwater (Staples et al., 2000). Moreover, considering their great hydrophobic nature, PAEs can be extensively adsorbed by organic and inorganic suspended particles in aquatic environments, then reach the bottom of this environment, and accumulate constantly in sediments (Chen et al., 2016). Therefore, sediments can also be a long-term contamination accumulation sink and a source of contaminants through suspension (Dobaradaran et al., 2017a, 2017b; Karbasdehi et al., 2016; Liu et al., 2014). Humans are also exposed to these toxic compounds through diet, bio-accumulation in the food chain, and extensive use or being subject to PAEs in different industrial objects through machining, storing, and transportation (Cheng et al., 2013). Therefore, comprehensive evaluation of distribution and accumulation of PAEs in aquatic sediments are essential for protecting and managing water environments, preserving the health of aquaculture as well as humans.

Asalouyeh (26°30′–27°50′ N, 51°01′–52°81′ N) is located in the northern side of the Persian Gulf coasts in Bushehr province, Iran. This region is well-known in the world due to the great project of Pars Special Energy Economic Zone (PSEEZ). PSEEZ has claimed around 100 km^2 of lands of Asalouyeh for different factories and industries. Progressive industrialization and fast growth of population in this region as the energy capital of Iran resulted in serious concerns over contamination problems in the coastal areas of this town. Development and accumulation of pollutants in the marine environment and movement of streams into the Persian gulf (West to East streams and vice versa in the coastal line) have caused the biodiversity cycle of the region to be constantly under threat (Arfaeinia et al., 2016). Although a limited number of studies have been done to investigate the contaminants in this region especially in the recent years. But most of these studies have been limited to measuring contaminants including heavy metals (Monikh et al., 2015) and oil compounds such as PAHs, PCBs, etc. (Arfaeinia et al., 2017a; Raeisi et al., 2016). To the best of our knowledge there is no data on distribution of PAEs in the sediments of coastal areas in the northern part of the Persian Gulf. Our study is the first report describing accumulation of sediments-bound PAEs in the northern part of the Persian Gulf. In the present study we aimed to (1) investigating the concentration, distribution, source, and ecotoxicological effects of PAEs and (2) evaluating the effect of regions with different land uses in distribution of these compounds in the sediments of the Asalouyeh-coasts.

2. Materials and methods

2.1. The studied region

The present study was performed in Asalouyeh Town, in the east of Bushehr province and in the margin of the Persian Gulf in the south of Iran. In recent decades, different gas and petrochemical industries have been established along with a set of light and heavy industries as well as support facility such as factories and warehouses in this town. It includes a complex of refineries and different petrochemical industries (Arfaeinia et al., 2016). In addition to petrochemical industries, various small and large industries including plastic making and production of polyethylene pipes, packaging industries, welding workshops, aluminum industry, etc. are also active in this area. Therefore, this region is of special importance and is considered as one of the important sources of contamination (Arfaeinia et al., 2017a; Raeisi et al., 2016). Furthermore, large areas of the lands in study area have been allocated to agriculture, and agricultural facilities such as the plastics for greenhouse agriculture, irrigation pipes, and packaging plastics that can also be other PAEs emission sources into the sediments (Monikh et al., 2013). In addition to industrial and agricultural activities, in urban regions also some activities including municipal services, wastewater treatment, animal husbandry, and breeding fish are other environmental concern in the study area.

2.2. Sample collection

Overall, 26 samples were collected from the surface sediments of coastal areas with different land uses in Asalouyeh town from Nov 2016 to Jan 2017. Seven sediment sampling stations were selected in the vicinity of industrial region (hereafter referred to as IS), 7 sampling stations in the vicinity of urban region (hereafter referred to as US), 7 sampling stations in the vicinity of agricultural fields (hereafter referred to as AGS), and 5 sampling stations in the vicinity of natural areas (hereafter referred to as NS) (Fig. 1). It should be noted that one of the sampling stations was located in the estuary of Khoor River into the sea. Ekman Steel Grab sampler device (25 * 25 * 25 cm^3) was used to collect the sediment samples. The collected samples were immediately placed inside glass amber containers pre-washed with n-hexane, and transferred to laboratory alongside dry ice at − 4 °C. In the laboratory, the samples were freeze-dried for 72 h, then passed through a 0.5 mm sieve, and kept at − 20 °C for further analyses.

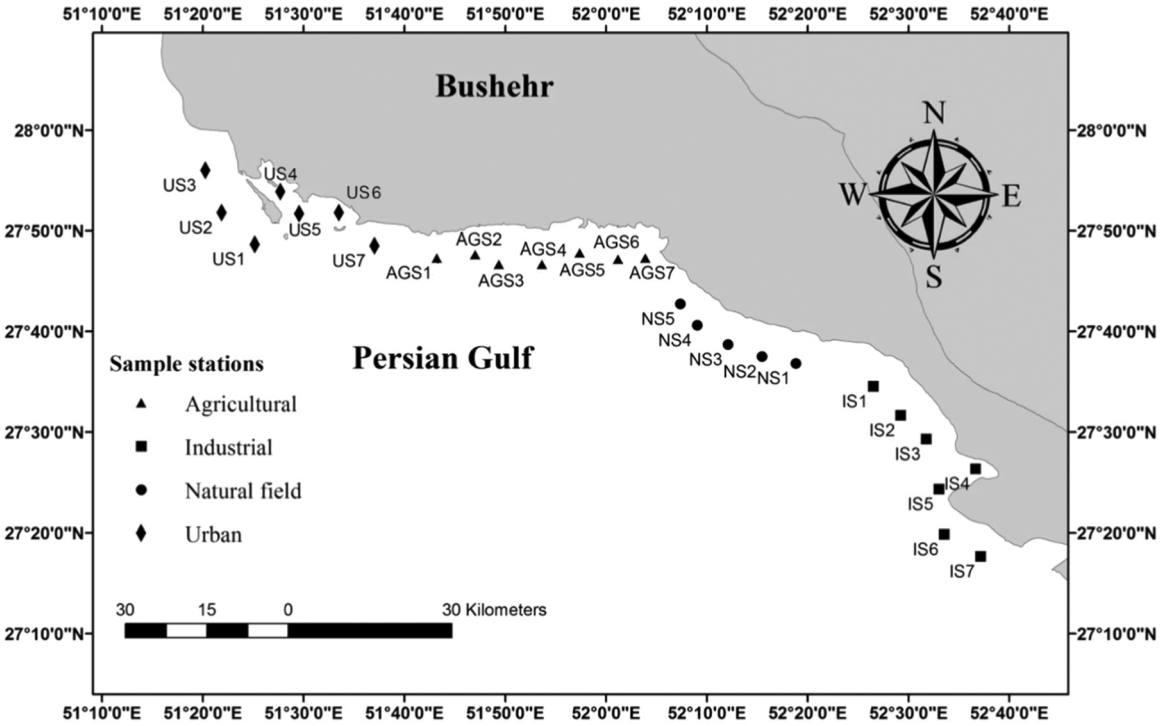

Fig. 1. The study area and sampling stations.

2.3. Physiochemical properties

The pH of the sediment samples was determined using a pH-meter (PHS-3C pH meter model, China). The electrical conductivity (EC) of the samples was measured by multiparameter U-50 (HORIBA, Germany) (Chai et al., 2015). To measure the total phosphorus content in the sediment samples, UV colorimetry method was used (Ruban et al., 1999). CHN analyzer (Perkin-Elmer, model 2400 CHN) was used to measure the total organic carbon content (Dargahi et al., 2015). The particle size analyzer (Mastersizer 2000, Malvern, Britain) was employed to analyze the distribution of the sediment sample particles with a capability of analyzing sizes between 0.02 and 2000 μm (Sochan et al., 2012). Further, the percentage of three fractions of particles including clay, silt, and sand was also determined.

2.4. Sample preparation

To extract PAEs from the sediment samples, the method presented by Chen et al. (2013) was used with some modification. In summary, 2 g of dry and homogeneous samples of sediments was taken and poured into clean centrifuge tubes. Thereafter, 6 ml of acetone/n-hexane solution with a 1:1 volumetric-volumetric ratio was added and then certain amounts of surrogate standard mixture solution (diisophenyl phthalate, di-n-phenyl phthalate, and di-n-benzyl phthalate controlling the) were added.

Samples were vortexed for 1 min, and then the mixture was placed inside ultrasonic device for 15 min. After that, the sample was centrifuged for 10 min at 2000 rpm to extract PAEs. After centrifugation, the organic layer containing the extracted compounds was withdrawn by a Pasteur pipette, and the sediments were extracted another two times with 6 ml of acetone/n-hexane solution (1:1 v/v). All extracts were then pooled together, to which activated copper was added for desulfurization. Next, the extract was dried over anhydrous sodium sulfate, and was then concentrated by a mind nitrogen flow to 0.6 ml. After that, the internal standard mixture (phenanthrene-d10, chrysene-d12) was added for analysis by gas chromatography with mass selective detection (GC/MSD).

2.5. Analysis

All samples were analyzed using gas chromatography- mass spectrometry (Agilent 7890 GC-5975 MSD) operating in electron impact and selective ion monitoring (SIM) mode using a capillary column for chromatographic separation. Helium with a very high purity degree (99.9999%) was used with a constant flow rate of 1.2 ml/min as carrier gas. The thermal program used was as follows: the column oven on 50 °C for 1 min and then with 15 °C/min, it reached 200 °C and was kept at this temperature for 1 min. Next, it was brought to 280 °C at 80 °C/min, and was kept at this temperature for 3 min. The samples were injected to the system with injector temperature at 250 °C in non-pulse and splitless states. The transfer line temperature was set at 280 °C, and the post-run temperature was adjusted as 285 °C for 2 min. PAEs concentration in the sediments was calculated based on dry weight.

2.6. Quality control and quality assurance

Firstly, to prevent any kind of potential contamination, no plastic equipment was used during the sampling and sample processing. Instead, glass materials were immersed in K_2CrO_4/H_2SO_4 solution, and washed with NaOH, deionized water, and acetone.

Parallel to the extraction of environmental samples, the control samples were also prepared with a similar process without sediment sample. A stock standard solution of 100 mg PAEs L^{-1} was prepared by diluting the original standard solution with acetone/n-hexane. The standard samples (with concentration levels of 0.5, 1, 5, 10, 20, 30, 40, 50 mg L^{-1}) for quality control were prepared by adding the standard solution to acetone/n-hexane with 1:1 (v/v) ratio. After that, the calibration curve was drawn for each PAE and calibration solutions were replaced every two weeks. In addition, spiked samples were also prepared by adding certain amounts of the standard solution to the samples. The devices were calibrated on a daily basis by calibration standards. A method blank, a spiked blank, a matrix spike, and replication of samples for each batch were performed on the samples. The mean recovery, limit of detection (LOD) and limit of quantification (LOQ) values for each of the PAE compounds were also determined by spiked

Table 1
The mean recovery, LOD and LOQ values for each PAE compound.

Compound	Mean recovery (%)	LOD (μg/g)	LOQ (μg/g)
DMP	89.7	0.007	0.023
DEP	92.6	0.009	0.029
DnBP	97.5	0.017	0.054
BBP	87.8	0.013	0.032
DEHP	96.3	0.022	0.069
DnOP	103	0.018	0.056
DiBP	111	0.009	0.030
DMGP	98.2	0.023	0.071
DMPP	87.5	0.008	0.026
DEEP	79.7	0.027	0.074
DnAP	67.5	0.012	0.036
DnHP	89.3	0.016	0.062
HEHP	97.4	0.011	0.035
DBEP	108	0.013	0.043
DCHP	103	0.017	0.057
DnNP	88.3	0.015	0.056

sample method prior to the analysis of samples. The data obtained are presented in Table 1. Finally, trace amounts were observed for some compounds in the method blank samples, with these values suitably subtracted from the values read in the samples.

2.7. Statistical analyses

The obtained results were statistically analyzed using SPSS for Windows version 19 (SPSS Inc., Chicago, IL). Shapiro-Wilk test was used to assessing the data normality. Significance of the relationship between the variables was examined by Fisher F-test. Spearman test was also applied to assess the correlation between PAEs levels and sediment properties and oceanographic factors. Furthermore, ArcMAP 10.3 (GIS) software was employed as a suitable instrument for plotting the distribution map of PAEs in the sediments along the northern part of the Persian Gulf. Finally, Principal component analysis (PCA) was also used as a statistical technique to estimate the possible sources of PAE compounds in the sediments.

3. Results and discussion

3.1. The effect of land use and physiochemical properties

Table 2 represents the physiochemical properties of sediment samples of Asalouyeh coasts in industrial, urban, agricultural, and natural regions. As can be observed, the clay content (particles smaller than 2 μm) lied within the range of 11.6–37.2% in the IS, 1.98–16.87% in the US, 7.34–38.74% in the AGS, and 6.4–26.7% in the NS. The silt content (particles between 2 and 75 μm) lied within the range of 23.43–61.32% in the IS, 27.37–75.3% in the US, 19.65–56.03% in the AGS, and 31–65.21% in the NS. The sand content (the fraction of particles higher than 75 μm) lied within the range of 18.03–57.045% in the IS, 19.93–56.2% in the US, 14.88–64.69% in the AGS, and 8.09–59.09% in the NS. This suggests that the dominant texture of the sediments in Asalouyeh includes sand and silt across all of the four regions. This can be due to the hybrid effect of anti-clockwise rotation and tidal fluctuations which caused the fine particles close to the mouth of estuaries to be to experience resuspension and then transferring them to the central part of the Gulf, and thus a larger fraction of particles remains in the coasts (Qiao et al., 2010).

It was also observed that the pH of the sediments in the IS, US, AGS, and NS areas has lied within the range of 5.65–7.12 (mean = 6.72), 6.94–7.75 (mean = 7.18), 6.78–7.45 (mean = 7.16), and 7.34–8.04 (mean = 7.69), respectively. The pH of the samples in the industrial and agricultural areas lies within the category of mild acidic to neutral, while in the urban and natural regions, it lies within the category of mild alkaline to neutral. The lower pH in the industrial and agricultural regions can be attributed to discharge of wastewaters containing large amounts of organic compounds. In response to the degradation of organic compounds, humic acid forms, which decreases the pH value (Nobi et al., 2010; Abdoallahzadeh et al., 2016). Furthermore, the higher pH in the natural area compared to other areas suggests that human activities including discharge of acid-containing industrial wastewater, use of fertilizer/organic amendments in the agricultural lands and urban parks, usage of pesticides, and fish breeding can acidify the sediments of the coasts (Jafari et al., 2018; Arfaeinia et al., 2017b).

Total organic carbon (TOC) concentrations lied within the ranges of 1.78–3.45% (mean = 2.51%), 1.21–3.42 (mean = 1.83%), 2.12–3.67 (mean = 3.15%), and 0.18–1.32 (mean = 0.54%) in the IS, US, AGS, and NS areas, respectively (Table 2). As can be seen, the order of TOC concentrations in the regions is as: industrial > agricultural > urban > natural. Among the urban stations, the maximum TOC level was observed in US6 station. This station is located in the estuary of a river called Khoor River, which receives large amounts of industrial wastewater rich in organic compounds. These findings show that human activities are the major source of carbon in the sediments of coasts, and can bring nearly a significant effect on carbon cycle processes in the coastal sediments (Li et al., 2014). Salinity lied within the range of 1.36–1.63 (mean = 1.49), 0.52–1.33 (mean = 0.95), 1.63–2.56 (mean = 1.91), and 0.08–0.21 (mean = 0.14) ds/m in IS, US, AGS, and NS areas, respectively (Table 2). With these results, the sediments of Asalouyeh town are categorized as non-saline materials (Du Laing et al., 2008).

Eventually, the phosphorus levels lied within the ranges of 178–370 (mean = 277), 370–630 (mean = 507), 365–472 (mean = 412), and 74–123 (mean = 99.1) μg/g in the IS, US, AGS, and NS areas, respectively (Table 2). As can be observed, the order of concentration of phosphorus in the sediments of different regions is as: US > AGS > IS > NS. Salinity is a key factor in distribution and speciation of phosphorus in sediment samples. With elevation of salinity, the extent of phosphorus desorption off the surface of sediment particles grows, thereby decreasing phosphorus content in the sediments (Deborde

Table 2
Physiochemical features of sediments from regions with different land use configuration in Asalouyeh Harbor.

Parameters	IS			US			AGS			NS		
	Min	Max	Mean ± SD	Min	Max	Mean ± SD	Min	Max	Mean ± SD	Min	Max	Mean ± SD
pH	5.65	7.12	6.72 ± 0.51	6.94	7.75	7.18 ± 0.21	6.78	7.45	7.16 ± 0.22	7.34	8.04	7.69 ± 0.27
TOC (%)	2.08	3.45	2.79 ± 0.50	1.21	3.42	1.79 ± 0.79	2.12	3.67	3.15 ± 0.51	0.23	1.32	0.70 ± 0.44
Salinity	1.38	1.55	1.46 ± 0.06	0.52	1.33	1.02 ± 0.32	1.63	2.56	1.91 ± 0.35	0.09	0.21	0.14 ± 0.04
TP[a] (μg/g)	178	310	242.86 ± 47.81	370	630	484.14 ± 104.05	365	472	412 ± 38.77	86	118	98.2 ± 14.77
Clay (%)	17.92	29.65	21.88 ± 4.58	4.80	15.65	11.57 ± 3.87	7.34	37.84	17.17 ± 9.93	7.20	12.34	10.24 ± 2.40
Silt (%)	23.43	61.32	40.77 ± 15.50	28.15	65.20	44.98 ± 13.36	19.65	56.05	36.37 ± 14.73	31	63.40	41.85 ± 13.5
Sand (%)	18.03	53.05	37.35 ± 14.61	19.93	56.20	43.45 ± 12.18	14.88	64.69	46.59 ± 19.31	24.26	59.09	47.91 ± 14.1

[a] Total Phosphorous.

et al., 2007).

3.2. The effect of land use and PAEs concentration

The individual concentration of the 16 PAEs compounds in the sediments collected from the IS, US, AGS, and NS areas are shown in Table 3. and the spatial distribution of Σ16PAEs is presented in Fig. 2. As seen, PAEs compounds were detected in all collected samples, suggesting that PAEs are among the ubiquitous contaminants in the studied region. The Σ16PAEs levels lied within the ranges of 74.42–94.01 (mean = 81.80), 10.22–25.34 (mean = 12.73), 52.17–62.51 (mean = 60.04), and 4.26–8.72 (mean = 5.56) μg/g in the IS, US, AGS, and NS areas, respectively. The mean concentrations of Σ16PAEs in the samples collected from IS and AGS areas are significantly higher than that of the US and NS areas ($P < 0.05$). The high PAEs values in the samples collected from IS environments can be due to the industrial wastewater and wastes released from large and small industries including petrochemical processes, gas refinement, electronic/electric equipment factories, chemical factories, industries that produce plastic pipes, and packaging industries (Nobi et al., 2010; Zheng et al., 2014). The results of this study are in agreement with another study in Beijing, China (Zheng et al., 2014). Zheng et al., reported that PAEs values in the samples collected from industrial environments have been higher than those of urban environments. The high PAEs values in the stations located in AGS region can be attributed to different cultivation activities including constructing greenhouse for vegetables, plastic mulching for cotton, apple packaging, and use of pesticides (Hongjun et al., 2013; Li et al., 2016). In addition, the water used for irrigation are supplied by some rivers around the region, which are contaminated by industrial discharge placed upward (Wang et al., 2014; Céspedes et al., 2006). Irrigation by contaminated water by wastewater even after the treatment may significantly increase the levels of toxic contaminants such as metals, PAEs, and polychlorinated biphenyls in soil (Hongjun et al., 2013). Confirming these results, in a research conducted by Niu et al. (2014) in China, it was found that use of plastic films, irrigation by wastewater, and chemical fertilizers are among the major sources of PAEs in agricultural lands. Furthermore, as seen in Table 3 and Fig. 2, among the stations located in the urban area, the maximum PAEs content has been found in US6 station. This station is situated in the intersection point of Khoor River and the Persian Gulf. These results indicate that PAEs have a transition pathway similar to other contaminants (e.g. toxic metals, PCBs, pesticides, polycyclic aromatic hydrocarbons (PAHs)), which are produced by human activities, and eventually transferred by the river, and accumulate in the sediments of coasts (Chen et al., 2017a; Dong et al., 2015).

Analysis of the composition (profiles of congeners) and individual concentrations of PAE compounds can assist in identifying the source, fate, and transfer of PAEs across environments. Detection frequency (DF) and relative contributions of the PAEs compounds are given in Fig. 3 and Fig. 4, respectively. Among the 16 studied PAEs compounds, DEHP had the maximum detection frequency and the highest relative contributions across all the regions. DEHP was detected (%100 frequencies) in all 26 samples collected from stations in different area. This compound had also the highest relative contribution of DEHP (about 30%) among all compounds in all the sampling areas (Fig. 4). The mean concentrations of DEHP in IS, US, AGS, and NS areas were 30.25 ± 4.75, 4.04 ± 0.52, 11.58 ± 1.18, and 1.99 ± 0.91 μg/g, respectively. Following this compound, DnBP, BBP, and DnOP had the highest concentrations. The detection frequencies of these compounds in the sampling sites were 95.12%, 87.8%, and 95.12%, respectively. The concentrations of DnBP in IS, US, AGS, and NS areas were 11.97 ± 0.67, 1.81 ± 0.65, 10.89 ± 1.36, and 0.92 ± 0.19 μg/g, respectively. For BBP, the values were 9.19 ± 0.52, 1.71 ± 0.84, 9.04 ± 1.05, and 1.18 ± 0.73 μg/g, respectively. Finally, the concentrations of DnOP in IS, US, AGS, and NS areas were 6.35 ± 0.83, 1.55 ± 0.76, 7.74 ± 0.84, and 0.86 ± 0.18 μg/g, respectively. This

Table 3
Individual concentrations (μg/g) of PAEs in sediments from regions with different land use configuration in Asalouyeh Harbor.

Area (n[a])	DMP	DEP	DnBP	BBP	DEHP	DnOP	DiBP	DMGP
IS (7)	5.68 ± 0.99	5.83 ± 0.53	11.97 ± 0.68	9.19 ± 0.52	30.25 ± 4.75	6.35 ± 0.83	2.50 ± 0.20	1.47 ± 0.15
US (7)	0.63 ± 0.55	0.89 ± 0.60	1.82 ± 0.65	1.70 ± 0.84	4.04 ± 0.52	1.55 ± 0.76	0.52 ± 0.41	0.21 ± 0.18
AGS (7)	3.69 ± 0.43	5.70 ± 0.49	10.89 ± 1.36	9.05 ± 1.06	11.58 ± 1.19	7.74 ± 0.849	3.64 ± 0.598	1.22 ± 0.27
NS (5)	0.19 ± 0.12	0.43 ± 0.08	0.91 ± 0.19	1.18 ± 0.73	1.99 ± 0.91	0.86 ± 0.18	0.33 ± 0.37	0.18 ± 0.02
DF[b] (%)	95.12	92.68	95.12	87.81	100.00	95.13	85.37	80.49

Area (n[a])	DMPP	DEEP	DnAP	DnHP	HEHP	DBEP	DCHP	DnNP	Σ16PAEs
IS (7)	0.19 ± 0.05	0.56 ± 0.06	1.05 ± 0.05	1.46 ± 0.07	0.47 ± 0.04	1.00 ± 0.02	2.30 ± 0.04	2.46 ± 0.89	81.70 ± 6.56
US (7)	0.09 ± 0.05	0.13 ± 0.07	0.19 ± 0.11	0.26 ± 0.18	0.14 ± 0.10	0.23 ± 0.14	0.29 ± 0.16	0.38 ± 0.26	12.73 ± 5.16
AGS (7)	ND	0.40 ± 0.08	0.84 ± 0.08	0.97 ± 0.07	0.15 ± 0.02	0.74 ± 0.05	1.67 ± 0.08	1.98 ± 0.10	60.04 ± 3.40
NS (5)	ND	ND	ND	ND	ND	ND	0.14 ± 0.04	0.21 ± 0.07	5.56 ± 1.61
DF[b] (%)	34.15	73.171	78.05	75.61	53.66	80.49	95.12	95.12	100.00

[a] The number of samples.
[b] Detection Frequency of PAEs compound in studied area.

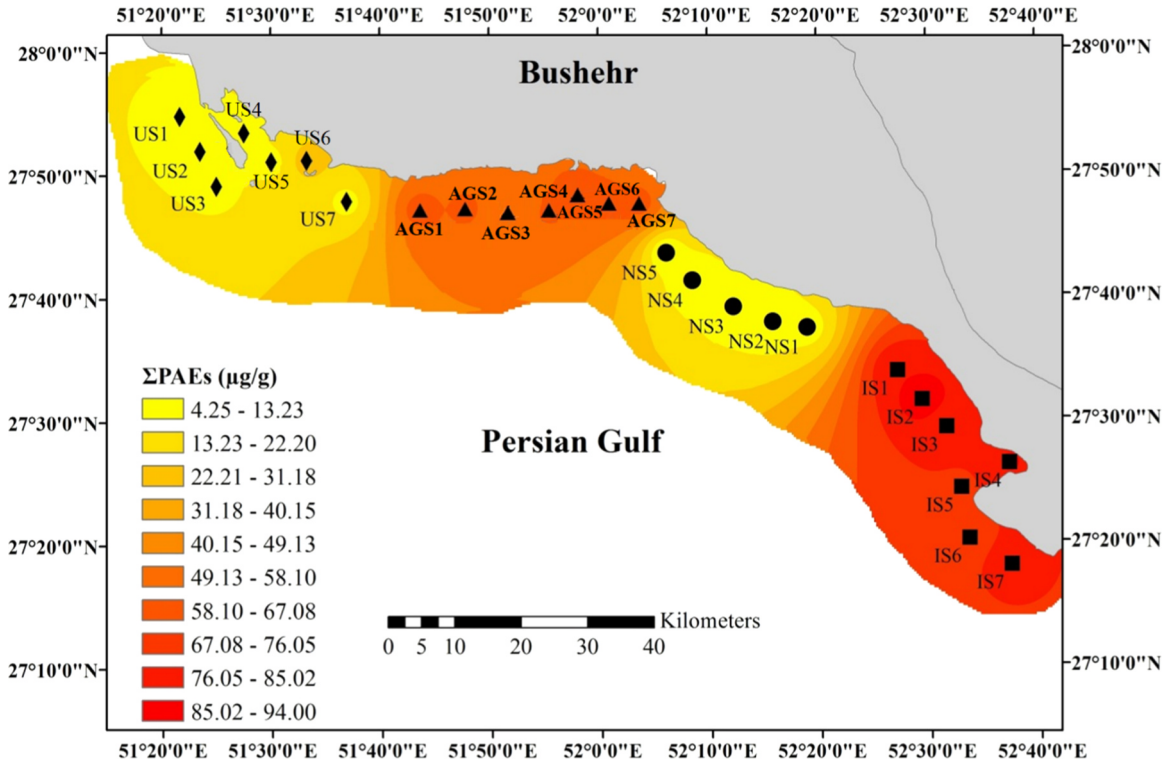

Fig. 2. The spatial distribution of Σ16PAEs (μg/g) in the coastal sediments of from regions with different land use in Asaluyeh.

pattern of distribution has been in accordance with previous studies, which have reported the dominant PAE compounds distributed across different environmental matrices (Wang et al., 2014; He et al., 2013). DEHP is the most common PAE compound, and accounts for nearly 50% of the industries output that produce PAEs in different countries including Canada, China, Malaysia, and European countries (Tan, 1995; Peijnenburg and Struijs, 2006; Lin et al., 2009; Wang et al., 2006). The high concentration level of this compound can be due to its high level of consumption and application as plastic additive, its heavy absorption by sediments, and its low degradability (Magdouli et al., 2013). The compounds with long alkyls or branched structures including DEHP, BBP, and DnOP are typically used as plasticizer in polymer industries to enhance the flexibility and handling properties of plastic products (Gomez-Hens and Aguilar-Caballos, 2003).

Identification of different congeners of PAEs in sediments and coastal waters can be used to pinpoint the possible sources of PAE contamination. In this regard, PCA was used as a statistical technique to determine the possible sources of PAE compounds in the sediments collected from the coasts of Asalouyeh harbor. The results of this analysis have been provided in Fig. 5. To simplify the obtained results, two principal components were extracted, accounting for 37.4% and 21.7% of the total variance, respectively. The first component (C1) is mostly related to DEHP, BBP, DnOP, di(2-n-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), di-nhexylphthalate (DnHP), and di-*n*-nonyl phthalate (DnNP), suggesting that this group of PAEs may have a shared source. The second component (C2) has been associated with DnBP, diisobutyl phthalate (DiBP), dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-amyl phthalate (DnAP), dimethylglycol phthalate (DMGP), di(2-ethoxyethyl) phthalate (DEEP), di(4-methyl-2-pentyl) phthalate (DMPP), and di(hexyl-2-ethylhexyl) phthalate (HEHP), which have possibly had a shared source. As seen in Fig. 5., the compounds in C1 are a series of compounds with long alkyl chain, suggesting that they originate from the plasticizers used in different chemical industries. C2 compounds consist of low molecular weight compounds. They essentially originate from usage of pesticides, fertilizers, and irrigation of agricultural lands with urban and industrial wastewater. As mentioned, in the studied regions, there are many large and small industries, which use different plasticizers and solvents for producing their products. Furthermore, in the agricultural lands present in this region, usage of different plastic films, polymer irrigation pipes, nylons utilized in greenhouse forms, etc. has grown progressively, which can be considered as a source of PAEs in the sediments of Asalouyeh harbor coasts. These results are in agreement with the findings reported by other researchers, who stated that the content of PAEs found in agricultural soils had a strong relationship with the extent of consumption of plastic films in agriculture. Furthermore, the level of these contaminants had a positive and significant relationship with the extent of consumption of plasticizers in chemical industries (Niu et al., 2014). Nowadays, although direct discharge of industrial waste and wastewater into the environment has decreased following strict regulations enacted by associated organization, PAEs in plastic compounds and other products are introduced into air, soil, water and other environment matrices. Subsequently, these contaminates are introduced into sediments through industrial and municipal effluents, surface runoff, and fine particle emitted from industrial, agricultural, residential applications.

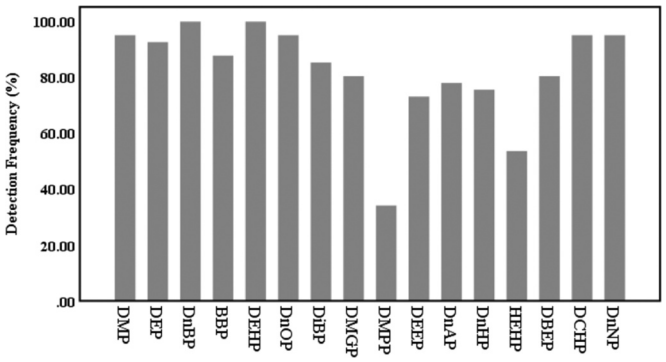

Fig. 3. Detection frequency of the PAEs compounds in the coastal sediments across the Asalouyeh Harbor.

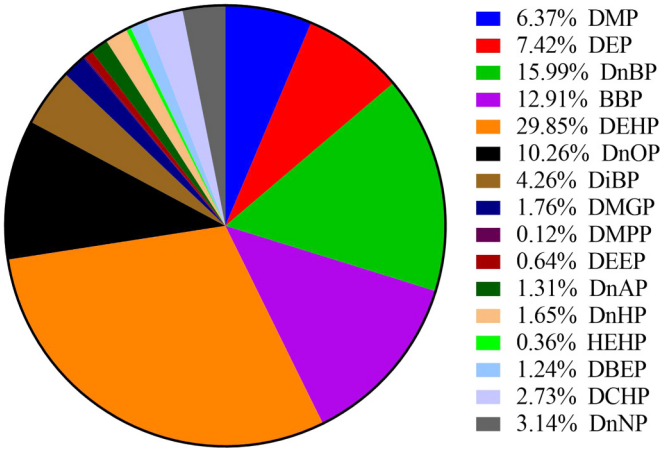

Fig. 4. Relative contributions of the PAEs compounds in the coastal sediments of Asalouyeh Harbor.

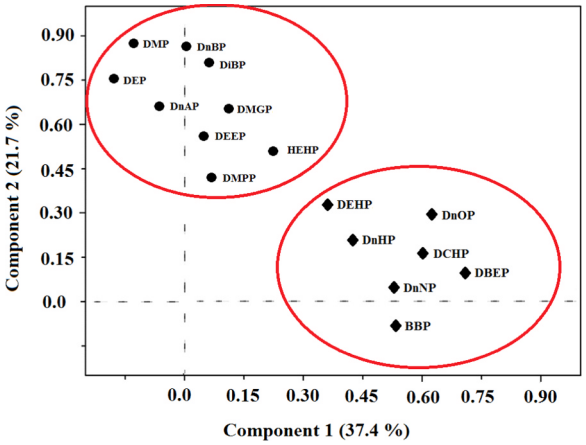

Fig. 5. Factor loadings of PAEs congeners on two principal components.

After that, they entered the coasts through industrial and urban effluents, surface floods, precipitation of dust from industrial environments, agricultural fields, factories and residential services, urban gardens and parks, etc., thereby accumulating in sediments. Surface runoffs and urban wastewaters in some regions are the main sources of entrance of PAEs into the coasts and their sediments (Zeng et al., 2008). Therefore, to control emission of PAE in these regions, suitable measures should be taken by the local authorities, to protect the quality of the river and marine environments and mitigate sediment contamination with PAE.

3.3. Sediment properties, oceanographic conditions and PAEs concentrations

The effects of sediment properties (TOC, size of particles (clay, silt, and sand), pH, EC, and total phosphorus content) and oceanographic conditions (average wave period (S), average wave height (cm) and maximum wave height (cm)) on PAEs concentration were examined by Spearman correlation analysis and the results are presented in Table 4 and Table 5. The results indicated that the oceanographic conditions (including average wave period (S), average wave height (cm) and maximum wave height (cm)) had no significant relationship with the concentration of PAEs species. These findings are inconsistent with the results of former reported studies, which reported that the combined effects of anti-clockwise circulation and tidal fluctuations caused the pollution-bounded sediments near the mouth of estuaries to be re-suspended and then carrying them to the central of the gulf (Qiao et al., 2010; Jiang et al., 2000). The results of this analysis also showed significant relationships ($p < 0.01$) between the fine fraction percentage of sediment particles with TOC, and Σ16PAEs. There was also a significant relationship ($p < 0.01$) between different species of PAEs. These results can be attributed to the high specific surface area of fine particles, where more active sites for adsorption are provided. Much contaminant and organic molecules are adsorbed easily onto the sites and subsequently their concentration are increased in sediments (Karbasdehi et al., 2016). Significant association between TOC and ΣPAEs was expected as it is well documented that hydrophobic organic matters will be mainly adsorbed into sediments through partition, which is in correlation with TOC content (Raeisi et al., 2016). In addition, the relationship between Σ16PAEs concentration and TOC values has been more significant than the relationship between Σ16PAEs concentration and size of particles. This implies that distribution of PAEs compounds is mostly affected by the organic content of sediments rather than the size of particles. This can be mainly be due to this fact that PAEs are a group of hydrophobic compounds and are quickly absorbed by the organic part of sediments, and finally accumulate (Magdouli et al., 2013). The strongest relationship ($p < 0.01$ and $R = 0.93$) was observed between Σ16PAEs and DEHP, suggesting that this compound can be a suitable marker substance for detecting Σ16PAEs in Asalouyeh sediments. A negative but significant relationship ($p < 0.01$) was also observed between pH value and total phosphorus content and TOC. Furthermore, a weak but significant relationship was seen between total phosphorus content and TOC. This suggests that at lower pH values, it causes diminished rates of anoxic degradation, resulting in enhanced accumulation of total phosphorus and organic part in the sediments (Jia et al., 2011). Furthermore, no significant relationships were observed between pH, EC, and Σ16PAEs, suggesting that pH and EC are not determinant parameters in the distribution of PAEs in sediments (Sun et al., 2013). Our findings were consistent with the results of former study in the southern Jiangsu Province in China, which stated that there is no correlations between the Σ6PAEs and pH of the sediments (Wang et al., 2014).

3.4. Evaluating the potential ecotoxicological effects

Due to the complexity of the contaminants composition in sediments, it is difficult to study the toxicity and risks of pollutants for organisms that are exposed to a certain pollutant (Chen et al., 2017b). Nevertheless, various studies have shown that some PAEs compounds including DEHP, DMP, DEP, BBP, and DnBP have bioaccumulation, toxic, and estrogenic effects for aquatic organisms (Ye et al., 2014; Kambia et al., 2001). Based on the sediment quality guideline (SQG) presented by Macdonald et al. (1996), the threshold effect level (TEL) and probable effect level (PEL) for DEHP was obtained as 182 and 2647 μg/g, respectively. DEHP concentration based on TEL and PEL can have the following three ranges of ecotoxicological effects: a) DEHP concentration less than TEL (with a low range of unlikely adverse biological effects), b) DEHP concentration values between TEL and PEL (with a low range of possible adverse biological effects), c) DEHP concentration values above PEL (with a high range of likely adverse biological effects). Based on the results of the present study, 100% of the samples collected from the IS, US, and AGS areas had the values higher than PEL. While in the NS area, 87.5% of the samples had the values in the range of TEL and PEL and the rest 12.5% had the values higher than PEL. This finding suggests that DEHP is a very common compound in the sediments of Asalouyeh harbor coasts and can have potential environmental effects on benthic creatures in the marine environments. In addition, the equilibrium partitioning theory by Verbruggen et al. (2001) was used to calculate the maximum permissible concentration (MPC) and Ecotoxicological Serious Risk Concentrations (SRC_{eco}) of PAEs. Comparison of the values of PAEs with MPC and SRC_{eco} are presented in Table 6. As seen, DMP concentrations has exceeded the MPC value in 100%, 100%, 12.5% and 0% of the

Table 4
Spearman correlation matrix between the measured parameters of sediment and phthalate esters in samples collected from the coastal areas in Asalouyeh.

Parameters	pH	EC	WC	TOC	TP	Sand	Clay + silt	DMP	DEP	DnBP	BBP	DEHP	DnOP	DiBP	DMGP	DMPP	DEEP	DnAP	DnHP	HEHP	DBEP	DCHP	DnNP	ΣPAEs
Ph	1.00																							
EC	0.18	1.00																						
WC	− 0.33*	0.20	1.00																					
TOC	− 0.49**	0.23	0.77**	1.00																				
TP	− 0.67**	0.08	0.19	0.26*	1.00																			
Sand	− 0.16	0.19	− 0.30*	− 0.49**	0.14	1.00																		
Clay + silt	0.16	− 0.19	0.30*	0.49**	− 0.14	− 1.00	1.00																	
DMP	0.07	0.17	0.09	− 0.07	0.08	− 0.07	0.07	1.00																
DEP	0.12	0.09	0.08	− 0.06	0.12	0.11	− 0.11	0.67**	1.00															
DnBP	− 0.16	0.11	0.07	0.15	− 0.07	0.13	− 0.13	0.43**	0.28*	1.00														
BBP	0.14	− 0.08	0.23	0.24	0.06	− 0.31*	0.31*	0.41**	0.18	0.09	1.00													
DEHP	0.11	0.11	0.56**	0.79**	0.14	− 0.47**	0.47**	0.84**	− 0.08	− 0.12	0.29*	1.00												
DnOP	0.07	0.08	0.34*	0.51**	0.16	− 0.37*	0.37*	0.61**	0.08	0.31**	0.41**	0.27*	1.00											
DiBP	− 0.11	0.05	0.11	0.08	0.12	0.09	− 0.09	0.32*	0.39**	0.13	0.33*	0.48**	− 0.08	1.00										
DMGP	− 0.05	− 0.07	0.31*	0.56**	0.09	− 0.38*	0.38**	0.19	0.41**	− 0.10	0.19	0.32*	0.12	0.21	1.00									
DMPP	0.08	− 0.08	0.21	0.34*	0.08	− 0.24	0.24	0.34*	0.06	− 0.06	0.32*	0.61**	0.13	0.14	0.39**	1.00								
DEEP	0.08	0.12	0.49**	0.61**	0.14	− 0.46**	0.46**	0.41**	0.13	0.48**	0.22	0.23	0.22	0.11	0.44**	0.13	1.00							
DnAP	− 0.10	0.11	0.44*	0.58**	− 0.07	− 0.34*	0.34**	0.12	− 0.10	0.14	0.48**	0.57**	− 0.11	0.09	0.23	0.12	0.07	1.00						
DnHP	0.06	− 0.08	0.42*	0.57**	− 0.09	− 0.29*	0.29*	0.18	0.31*	0.27*	0.11	0.10	0.08	0.09	0.18	0.22	0.11	0.31*	1.00					
HEHP	0.11	− 0.16	0.39*	0.57**	− 0.07	− 0.19	0.19	0.19	0.34*	0.43**	0.32*	0.49**	− 0.06	0.19	0.27*	0.14	0.12	0.19	0.14	1.00				
DBEP	− 0.05	0.12	0.27*	0.48**	− 0.13	− 0.23	0.23	0.23	0.41**	0.08	0.18	0.23	0.18	0.22	0.23	0.13	0.09	0.28*	0.21	− 0.08	1.00			
DCHP	0.08	0.11	0.28*	0.44**	0.12	− 0.27*	0.27*	0.19	0.33*	0.13	0.42*	0.18	0.22	0.18	0.31*	0.18	0.21	0.27*	0.17	0.20	− 0.10	1.00		
DnNP	− 0.02	0.09	0.47**	0.61**	0.17	− 0.09	0.09	0.17	0.18	0.32*	0.09	0.06	0.22	0.15	0.09	0.09	0.18	0.43**	0.19	0.21	− 0.08	0.11	1.00	
ΣPAEs	0.07	− 0.13	0.43**	0.81**	0.24	− 0.26*	0.26*	0.53**	0.41**	0.69**	0.67**	0.93**	0.23	0.17	0.41**	0.14	0.23	0.28	0.34*	0.37*	0.19	0.21	0.17	1.00

* Correlation is significant at $p < 0.05$ (two-tailed).
** Correlation is significant at $p < 0.01$ (two-tailed).

Table 5
Spearman correlation matrix between the oceanographic conditions and PAEs concentration in samples collected from the coastal areas in Asaluyeh.

Parameters	DMP	DEP	DnBP	BBP	DEHP	DnOP	DiBP	DMGP	DMPP	DEEP	DnAP	DnHP	HEHP	DBEP	DCHP	DnNP	ΣPAEs
Average wave period	0.08	0.16	0.23	0.18	0.22	0.23	0.13	0.09	0.22	0.11	− 0.08	0.22	0.14	0.27	0.17	0.14	0.19
Average wave height	0.18	0.09	0.13	− 0.07	0.25	0.19	0.27	− 0.11	0.05	− 0.19	0.13	0.09	0.13	0.08	0.22	0.18	0.08
Maximum wave height	− 0.11	0.24	0.11	0.13	0.12	0.22	− 0.09	0.32*	0.18	0.22	0.23	0.20	0.09	0.27	− 0.21	0.09	0.11

* Correlation is significant at $p < 0.05$ (two-tailed).

Table 6
Comparison of the values of PAEs with MPC and SRC_{eco}.

PAEs compound	DMP	DEP	DiBP	DnBP	BBP	DEHP	ΣPAEs
MPC	1	94	0.092	2.1	1.4	1	1.4
SRC_{eco}	84	580	17	36	48	10	57
Percentage of samples higher than MPC (%)							
IS	100	0	100	100	100	100	100
US	12.5	0	81.8	90.9	36.36	100	100
AGS	100	0	100	100	100	100	100
NS	0	0	50	0	12.5	100	100
Percentage of samples higher than SRCeco (%)							
IS	0	0	0	0	0	100	100
US	0	0	0	0	0	0	0
AGS	0	0	0	0	0	14.5	85.7
NS	0	0	0	0	0	0	0

samples collected from IS, AGS, US, and NS areas respectively. However, it has been less than SRC_{eco} across all of the samples. But DEP concentrations did not exceed the MCP and SRC_{eco} in all stations. DiBP concentrations exceeded MPC value in 100%, 100%, 81.8%, and 50% of the samples taken from IS, AGS, US, and NS areas, respectively. However, DiBP concentrations did not exceed the SRC_{eco} in all stations. DnBP has also exceeded MPC values in the samples taken from IS, AGS, US, and NS areas in 100%, 100%, 90.9%, and 0% of cases, respectively, though it has not been higher than SRC_{eco} in all samples. BBP concentrations were higher than MPC value in the samples collected from IS, AGS, US, and NS areas in 100%, 100%, 36.36%, and 0% of samples, respectively; though it was lower than SRC_{eco} in the samples collected from all the areas. High DEHP concentrations in the samples taken from the sediments of Asalouyeh harbor coasts have caused its values to be higher than MPC in all collected samples. Furthermore, in 100%, 14.25%, 0%, and 0% of cases, the samples taken from IS, AGS, US, and NS areas exceeded SRC_{eco} value, respectively. Comparing the concentrations obtained for Σ16PAEs with MPC and SRC_{eco} values, it was observed that Σ16PAEs concentrations were higher than MPC in 100% of the samples collected from all of the four studied areas. Furthermore, Σ16PAEs concentrations were higher than SRC_{eco} in 100%, 100%, 87.50%, and 0% of the samples in IS, AGS, US, and NS areas, respectively. Based on the obtained results, it should be noted that the entrance of phthalate-containing materials into Asalouyeh harbor coasts should be strictly controlled.

In addition, previous studies suggested that if the contaminant concentration exceeds the environmental risk levels (ERL), it may cause numerous adverse effects on the quality of the environment and human health. In the study by Van Wezel et al. (2000), ERL has been reported for nearly 150 compounds. In this study, based on the environmental chemistry and ecotoxicology, for DEHP and DnBP compounds in sediments, ERL levels were expressed as 0.7 and 1 μg/g, respectively. The median concentration of DEHP in 100% of the samples collected from the sediments of Asalouyeh harbor coasts has exceeded ERL limit. The median concentration of DnBP has also exceeded ERL level in all samples collected from the IS, US, and AGS areas. In the NS area, except for the sample taken from NS4, the median concentration of DnBP exceeded 0.7 μg/g. Toxicological studies have shown that BBP and DiBP have also similar effects on testicles and reproduction. As ERL values have not been presented for these two compounds, thus in this study, the ERL value presented for DnBP (0.7 μg/g) was also employed to evaluate the ecotoxicological effects of these compounds. With regards to BBP, its concentration was higher than 0.7 μg/g in 100% of the samples taken from IS and AGS areas. However, in the US and NS areas, BBP concentration exceeded ERL limit in 72.5% and 12.5% of the samples, respectively. DiBP concentration were also higher than 0.7 μg/g in 100% of the samples collected from the IS and AGS areas. In the US area, except for the sample taken from US6 which is located in the estuary of Khoor River, in the rest of cases DiBP concentration were lower than ERL. Finally, in the NS area, DiBP concentration has not exceeded the ERL in whole of samples. The findings of this study showed that the sediments of Asalouyeh harbor sediments are heavily contaminated with PAEs. This situation can have extremely negative effects on the composition of microbial populations, enzymatic activities, as well as micro and macro organisms in the marine environment. Overall, as accumulation of PAE compounds in seawaters and sediment creatures can eventually be transferred to consumers in the top of the food chain, presence of these compounds is really serious (Wang et al., 2014). Similarly, as these contaminants may have long-term effects in coastal sources and threaten human life (Kelly et al., 2007), thus special attention should be considered by authorities to protect the marine ecosystems in this region.

4. Conclusion

This study has provided the primary data on the concentration level of PAEs in the sediments of Asalouyeh harbor in areas with different landuses including industrial, urban, agricultural, and natural field. The findings showed that PAEs are ubiquitous environmental contaminants in this region, and the main compounds were DEHP, DnBP, BBP, and DniP. It was also observed that the mean concentrations of Σ16PAEs were significantly higher in the IS and AGS areas, compared with US and NS areas. The concentration of PAE compounds had a positive and significant relationship with TOC, suggesting that the distribution of PAEs in the sediments of Asalouyeh coasts is heavily influenced by the organic content of the sediments. Furthermore, there was a significant relationship between Σ16PAEs and DEHP. Therefore, DEHP can be used as a suitable marker substance for identifying Σ16PAEs in the sediments. Plasticizers and solvents used in different chemical industries, application of pesticides, fertilizers, different plastic films, and polymer irrigation pipes in greenhouse fields were among the major sources of PAEs in the sediments of studied coasts. In terms of ecotoxicological effects, it was observed that different compounds of PAEs especially DEHP exceeded the hazardous environmental levels presented by various organizations. They can have extremely negative ecotoxicological effects on the ecology, composition of the live aquatic populations, enzymatic activities, and the micro and macro organisms of marine environment. Therefore, it is highly suggested to prevent discharging of wastes containing PAEs into the coasts. These results here, provide a complete knowledge on the situation of PAEs contamination as well as its ecotoxicological risks in the sediments of the region with different land uses. Nevertheless, in this study, the bioavailability and bioaccessibility of PAEs have not been considered in the risk assessment and

can be a good point for next study. Finally, further and comprehensive studies on bioaccumulation of PAEs in aquatic organisms and plants exist in the food chain are required to analysis risk assessment of these hazardous contaminants, as a principal action for protecting the sediments.

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